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FORM PTO-1: (REV 10-2000	90 U.S. DEPAR	TMENT OF COMMERCE PATER	NT AND TRADEMARK OFFICE	ATTORNEY'S DOCKE				
TF	ANSMITTAL LETTER		P/37					
	DESIGNATED/ELECT	,	U.S. APPLICATION NO	0. (If known, see 37 CFR 1.5)				
	CONCERNING A FILI		0776	30478				
	ATIONAL APPLICATION NO. /EP99/08055	INTERNATIONAL: 25 Octobe		PRIORITY DATE 30 Octo	CLAIMED ber 1998			
PR	OF INVENTION OCESS AND CONVERTI	ER FOR THE	PREPARATION (	F AMMONIA				
APPLICA	ANT(S) FOR DO/EO/US	Christia	n SPETH					
Applican  1	2. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.  3. This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).  4. The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).							
_	PCT Article 36 (35 U.S.C. 371(c)(5)). including amended claims.							
Items I	ems 11 to 16 below concern document(s) or information included:							
11.	An Information Disclosure Statement under 37 CFR 1.97 and 1.98.							
12.	An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.							
13. X	A FIRST preliminary amendment.							
	A SECOND or SUBSEQUENT I	preliminary amendm	ent. EXPRESS N	IAIL CERTIFIC.	ATE			
14.	A substitute specification.				spondence is being			
15.	A change of power of attorney at			deposited with the United States Postal Service as E Mail Post Office to Addresses (mail label				
16. <b>X</b> X	Other items or information:  2 sheets of drawi.	ngs.	Asst. Commissioner fon April 26	or Patents, Wash				
	Print EFS form.		-Dorothy	Jenkins				
			Name of Per	son Mailing Cor	$\nu$			

Signature April 26, 2009 Date of Signature

			<b>JC</b> 18 P	lec'c	PCT/PTO	2 6 APR :
& APPLICOO 90.0	830478	INTERNATIONAL APPLICATION NO. PCT/EP99/08055			ATTORNEYS DOCK	ET NUMBER
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BASIC NATION Neither interm nor internatio and International USPTO but In International international International International International	AL FEE (37 CFR 1.492 attional preliminary examinal search fee (37 CFR 1 and Search Report not proper liminary examination atternational Search Repopreliminary examination search fee (37 CFR 1.44 preliminary examination	(a) (1) - (5): imation fee (37 CFR 1.482) .445(a)(2)) paid to USPTO epared by the EPO or JPO free (37 CFR 1.482) not paid to rt prepared by the EPO or JPO ee (37 CFR 1.482) not paid to US (sa)(2)) paid to USPTO fee paid to USPTO (37 CFR 1.482)	PTO but <b>\$710.00</b> 82)			
International	preliminary examination	s of PCT Article 33(1)-(4) fee paid to USPTO (37 CFR 1.4: PCT Article 33(1)-(4)	82)			
and an claims	-	OPRIATE BASIC FEE AN		s	860.	
	earliest claimed priority		20 30	s		
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE			
Total claims	10 -20		X \$18.00	s		
Independent claims	2 -3:		X \$80.00	S		
MULTIPLE DEPI	ENDENT CLAIM(S) (if ap		+ \$270.00	S		
	TOTA	L OF ABOVE CALCULA	TIONS =	\$	860.00	
are reduced Processing fee of	Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.  SUBTOTAL =  recessing fee of \$130.00 for furnishing the English translation later than 20 30					
months from the	earliest claimed priority		+	Η.		
		TOTAL NATION t (37 CFR 1.21(h)). The assignm et (37 CFR 3.28, 3.31). \$40.00 p	ent must be	s	860.00	
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a.   A check in the amount of \$ 860. to cover the above fees is enclosed. Check No. 4410  b. Please charge my Deposit Account No. in the amount of \$ to cover the above fee A duplicate copy of this sheet is enclosed.  c.   The Commissioner is bereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0700. A duplicate copy of this sheet is enclosed.						
NOTE: When 1.137(a) or (b) SEND ALL CORRE OSTROLES	re an appropriate time  i)) must be filed and gra	imit under 37 CFR 1.494 or 1.4 inted to restore the application  SOFFEN, LLP	95 has not been	met,	a petition to re	
			Edwa	ard	A. Meilr	nan
New Yor	c, NY 10036-8	403	NAME			

24,735 REGISTRATION NUMBER

Tel: (212) 382 0700

d PCT/PTU 2 6 APR 200 P/3781-4

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE					
In re Patent Application of					
Christian SPETH	Date: A	pril 26, 2001			
Serial No.:	Group A	at Unit:			
Filed:	Examine	er:			
For: PROCESS AND CONVERTER FOR THE PRI	EPARATION (	OF AMMONIA			
Asst. Commissioner for Patents					
Washington, D.C. 20231					
Washington, D.C. 20231					
AMENDMENT/S	UBMISSION				
Prior to examination, please amend the application	ation as follows	5.			
FEE CALCULATION					
Any additional fee required has been calculate	d as follows:				
If checked, "Small Entity" state	ıs is claimed.				
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NO. CLAIMS HIGHEST NO.					
AFTER PREVIOUSLY				ADDIT.	
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FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAI		(\$40 SE or \$80) (\$135 SE or \$270)	\$ \$		
* not less than 20 ** not less than 3		TOTA	L \$		
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In the event the actual fee is greater than the payment submitted or is inadvertently not enclosed or if any additional fee during the prosecution of this application is not paid, the Patent Office is authorized to charge the underpayment to Deposit Account No. 15-0700.

### CONTINGENT EXTENSION REQUEST

If this communication is filed after the shortened statutory time period had elapsed and no separate Petition is enclosed, the Commissioner of Patents and Trademarks is petitioned, under 37 C.F.R. §1.136(a), to extend the time for filing a response to the outstanding Office Action by the number of months which will avoid abandonment under 37 C.F.R. §1.135. The fee under 37 C.F.R. § 1.17 should be charged to our Deposit Account No. 15-0700.

### AMENDMENTS

- \_X\_ If checked, amendment(s) to the specification and/or claims are submitted herewith.
- 1. \_\_\_ If checked, an abstract is submitted as the last page of Appendix A.

### 3. Claims:

Please amend claims 4 and 5 and add new claims 9 and 10 pursuant to 37 C.F.R. § 1.121(c)(i) as set forth in the "clean" version attached hereto as Appendix A. Entry is respectfully requested. A version with markings to show the changes made pursuant to 37 C.F.R. § 1.121(c)(ii) is attached hereto as Appendix B.

\_\_\_\_ If checked, the optional complete set of "clean" claims pursuant to 37 C.F.R. § 1.121(c)(3) is attached hereto as Appendix C.

00506861.1

### REMARKS/ARGUMENT

This Preliminary Amendment is being submitted to change the multiple dependent claims to single dependent claims in order to reduce the government filling fee.

# EXPRESS MAIL CERTIFICATE

I hereby certify that this correspondence is being deposited with the United States Postal Service as Express Mail to Addressee (mail label # EL613112673US) in an envelope addressed to: Asst. Commissioner for Patents, Washington, D.C. 20231, on April 26, 2001:

Dorothy Jenkins

Name of Person Mailing Correspondence

April 26, 2001

Date of Signature

Respectfully submitted,

Edward A. Meilman

Registration No.: 24,735

OSTROLENK, FABER, GERB & SOFFEN, LLP

1180 Avenue of the Americas New York, New York 10036-8403

Telephone: (212) 382-0700

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#### APPENDIX A

# "CLEAN" VERSION OF EACH PARAGRAPH/SECTION/CLAIM 37 C.F.R. § 1.121(b)(ii) AND (e)(i)

# CLAIMS (with indication of amended or new):

- (Amended) 4. The process of claim 2, wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.
- (Amended) 5. The process of claim 2, wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.
- (New) 9. The process of claim 3, wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.
- (New) 10. The process of claim 3, wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.

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# APPENDIX B

# VERSION WITH MARKINGS TO SHOW CHANGES MADE

37 C.F.R. § 1.121(b)(iii) AND (c)(ii)

# CLAIMS:

- 4. The process of claim 2 [and 3], wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.
- 5. The process of claim 2 [and 3], wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.

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- 1 -

# Process and Converter for the Preparation of Ammonia

The present invention relates to the preparation of ammonia by catalytic conversion of ammonia synthesis gas.

More particularly, this invention concerns synthesis of ammonia at high conversion rates of ammonia synthesis gas in presence of an ammonia synthesis catalyst arranged in a tubular reaction zone being cooled by a cooling agent on shell side of the tubular reaction zone. Synthesis of ammonia from synthesis gas of hydrogen and nitrogen is an exothermic process and the process requires cooling to obtain high conversion rates.

Even if the concentration of hydrogen and nitrogen in the synthesis gas is close to the stoichiometric composition for ammonia formation, complete reaction to ammonia cannot be obtained by a single passage of the synthesis gas through a catalytic bed. Furthermore, due to the exothermic nature of the ammonia synthesis, increasing temperature during passage through the catalytic bed displaces the equilibrium concentration towards lower ammonia concentration. Several methods for cooling the ammonia synthesis process are known.

The usual methods for the preparation of ammonia from synthesis gas employ either indirect or direct cooling of the synthesis gas between a number of catalytic beds, wherein the ammonia synthesis passes over an ammonia synthesis catalyst.

By direct cooling, cold synthesis gas is introduced into partly reacted synthesis gas between the beds. The disadvantage of this cooling method is dilution of the partly reacted gas with unreacted gas resulting in lower ammonia concentration in the product stream from the process.

By the indirect cooling method, partly reacted synthesis gas is cooled by cold gas, usually fresh synthesis gas in a heat exchanger arranged between outlet and inlet of two catalyst beds.

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It has now been found that conversion rate of ammonia synthesis gas to ammonia is much improved when cooling the synthesis gas as it proceeds through a catalytic bed of ammonia synthesis catalyst by heat transfer to a cooling agent being in continuous heat contact with the process.

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Accordingly, this invention provides a process for the preparation of ammonia comprising steps of:

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contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes;

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cooling the reaction zone continuously by transferring heat from the reaction zone to a cooling agent; and

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withdrawing an ammonia rich effluent stream from the reaction zone.

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In its most general embodiment, the above process is carried out in a converter with one or more catalyst tubes arranged in a shell for retaining a cooling agent. Synthesis gas is introduced at top of the catalyst tube and passed through the reaction zone of an ammonia synthesis catalyst. Heat being developed during conversion of hydrogen and nitrogen contained in the synthesis gas to ammonia is continuously transferred through wall of the catalyst tube to the cooling medium surrounding the tube. By continuous cooling of the process, an adiabatic temperature

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increase is substantially avoided, so that the process is carried out at substantially isothermal conditions. Isothermal conversion of the synthesis gas results in higher conversion rates of the gas to ammonia than in the known ammonia synthesis processes with indirect or direct cooling of partially reacted synthesis gas, where the cooled gas is contacted with the catalyst at adiabatic conditions. Having removed heat of reaction from the reaction zone, the cooling medium is continuously or periodically withdrawn from the converter and externally cooled by e.g. heat exchange with water or steam and recycled to the converter by conventional means.

In a specific embodiment of the invention, the cooling agent is retained in a space formed by outer wall of the catalyst tube and inner wall of a cooling tube concentrically surrounding the catalyst tube.

As an advantageous feature of the latter embodiment, shell of a reactor with a number of catalyst tubes can be avoided or made from material with considerably lower mechanical strength than in the conventional ammonia converters.

Preferably, the cooling tubes surrounding the catalyst tubes are designed with a lower mechanical strength than the catalyst tube. In case of catalyst tube rupture reacting gas escaping at high pressure into the cooling tubes, ventilates into a space outside the cooling tube. Thereby, the synthesis gas depressurizes outside the cooling tubes and detrimental reactions of the gas with the cooling agent are avoided advantageously.

A further object of the invention is to provide a converter for the preparation of ammonia by reaction of ammonia synthesis gas in presence of an ammonia synthesis catalyst and

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cooling the reaction as it proceeds through the synthesis catalyst, the converter comprises at least one catalyst tube adapted to receive the ammonia synthesis gas and to hold a reaction zone with the ammonia synthesis catalyst, which at least one catalyst tube being arranged in a container with a cooling agent, as schematically shown in the attached Fig. 1.

Cooling media being useful as cooling agent in the above process and reactor will be any solid or liquid having a melting or boiling point below the desired temperature in the reaction zone, including salt or mixture of salts, metals or liquids being inert at the actual process conditions. Those cooling agents include eutectic mixtures of salts like mixtures of KNO3, NaNO3 and NaNO2 (supplied by Degussa) and eutectic mixtures of NaOH and KOH. Further eutectic salt mixtures and cooling liquids are well known in the chemical industry. The usual temperature condition in the above process will be between 300°C and 600°C. The temperature of the cooling agent has to be maintained at a predetermined level within the operation temperature range by external cooling of the agent as mentioned herein before.

Removal of ammonia from the ammonia rich product gas being withdrawn from the catalyst tubes is further an embodiment of the invention obtained through adsorption on an adsorbent having high affinity to ammonia at high pressure, such as regeneration of the spent adsorbent is carried out through depressurization of the adsorbent and recovery of ammonia rich gas similar to separation of e.g. oxygen or nitrogen in the known pressure swing adsorption processes. Furthermore, ammonia may be separated from unconverted synthesis gas by cooling and condensation of ammonia in the

ammonia rich effluent stream from the process. Unreacted synthesis gas being separated from ammonia in the product gas may then be recycled to the catalyst tube or passed to a subsequent catalyst tube for further conversion, as schematically shown in Fig. 2 and Fig. 3.

### Example

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In a specific embodiment of the present invention a synthesis feed gas at a pressure of 13.8 MPa is preheated to 350°C and introduced to a reactor furnished with 600 reactor tubes with an inner diameter of 80.1 mm. The tubes were loaded with an upper portion of conventional iron ammonia catalyst and a lower portion of conventional ruthenium ammonia catalyst. Synthesis gas is distributed to the tubes and reacted over the ammonia catalyst. The catalyst tubes are surrounded by a shell. In the space between the shell and the tubes, a salt melt is being circulated countercurrently to the gas flow direction inside the tubes and in heat conducting relationship with the synthesis. Circulation of the salt melt serves to remove heat evolved from the exothermic ammonia synthesis reaction. The salt melt is introduced at 360°C into the cooling space and leaves the reactor at 420°C. The hot melt is cooled outside the reactor to 360°C in a heat exchanger, in which the heat desorbed from the salt melt is used for preheating of synthesis gas. The cooled salt melt is then pumped back to the reactor. Having passed through the catalyst reacted synthesis gas, being rich in ammonia, leaves the tubes and is withdrawn from the reactor. The gas is cooled by heat exchange with fresh synthesis gas.

In Table 1 below are listed the concentrations of the components in the gas stream inlet and exit the reactor as obtained by the above experiment.

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Table 1

	Inlet gas	Exit gas
Composition (mole%):		
H <sub>2</sub>	73.59	52.95
$N_2$	25.37	18.73
Ar	0.36	0.45
CH <sub>4</sub>	0.68	0.87
NH <sub>3</sub>		27.00
Pressure, MPa		13.4
Temperature, °C	13.8	402
	350	

The inventive process may be employed in a one through ammonia synthesis section as well as in a more conventional type ammonia synthesis loop section or in combination with similar or other ammonia converter types in more advanced ammonia synthesis loop sections e.g. comprising feed gas converters and/or purge gas converters. The ammonia product may be retrieved from the ammonia rich product gas in the synthesis section by cooling and condensation of ammonia in the ammonia rich effluent stream or absorption. The removal of ammonia may be conducted in one or more stages, between and/or after each of the reaction zones.

International Patent Application No. PCT/EP99/08055 Applicant: HALDOR TOPSOE A/S PCT 1083 – 00989/ej November 10, 2000

### Claims 1 to 8

A process for the preparation of ammonia comprising the steps of

contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as a reaction zone in one or more catalyst tubes;

cooling the reaction zone by a heat conducting relationship with a cooling agent; and

withdrawing an ammonia rich effluent stream from the reaction zone;

wherein the cooling agent is selected from salts, mixtures of salts and metals having a melting point below the temperature in the reaction zone.

- The process of claim 1, wherein the ammonia synthesis gas is contacted with the ammonia synthesis gas arranged in two or more reaction zones with intermediate withdrawal of an ammonia rich effluent stream between the reaction zones.
- The process of claim 1, wherein the ammonia rich effluent stream is separated in a stream of unconverted ammonia synthesis gas and an ammonia product stream, the unconverted ammonia synthesis gas is recycled to the reaction zone.
- The process of claim 2 and 3, wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia
- The process of claim 2 and 3, wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.

- The process of claim 1, wherein the cooling agent is circulated within cooling tubes, each surrounding concentrically one catalyst tube.
- A converter for the preparation of ammonia comprising at least one catalyst tube adapted to receive ammonia synthesis gas and to hold a reaction zone of ammonia synthesis catalyst; and
  - at least one cooling tube concentrically surrounding the at least one catalyst tube and being adapted to hold the cooling agent selected from salts, mixtures of salts and metals having a melting point below the temperature in the reaction zone.
- The converter of claim 7, wherein the wall of the cooling tube(s) has a lower mechanical strength than the wall of the catalyst tube(s).

### ABSTRACT

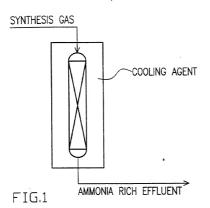
# Process and Converter for the Preparation of Ammonia

5 Process for the preparation of ammonia comprising steps of

contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes;

cooling the reaction zone by heat conducting relationship with a cooling agent; and

withdrawing an ammonia rich effluent stream from the reaction zone.



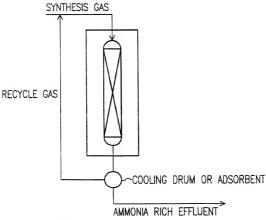


FIG.2

# 2/2

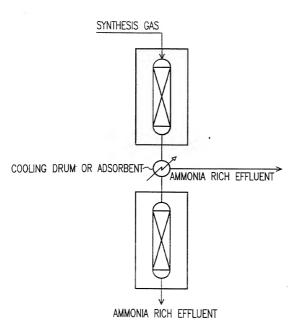


FIG.3

oFGS FILE NO. P/3781-4

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or a joint inventor (if plural inventors are named) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PROCESS AND CONVERTER FOR THE PREPARATION OF AMMONIA

the specification of which is attached hereto, unless the following box is checked:

was filed on 25 October 1999 as United States patent Application Number or PCT International patent

application number PCT/EP99/08055 and was amended on 10 November 2000

I leighby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendigated referred to above.

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Reknowledge the duty to disclose all information known to be material to patentiating in accordance with a large of the day to disclose all information known to be material to patentiating in accordance with a large of the day of the large of the day of the large o

Prior Foreign or Provisional Application(s)

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COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. 119	
Denmark	1998 01398	30 October 1998	YES X NO	
			YES NO	

I hereby claim the benefit under Title 35. United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §117, J. acknowledge the duty to disclose information which is material to patentiability as defined in Title 57, Code of Federal Regulations, §1.56 which became available between the filling date of the prior application and the national or PCT international filling date of this application.

UNITED STATES APPLICATION NUMBER	DATE OF FILING (day, month, year)	STATUS (patented, pending, abandoned)

I hardw appoint customer no. 2352 OSTROLENK, FABER, GERB & SOFFEN, LLP, and the members of the firm, Samuel H. Weiner - Reg. No. 18,510; Jorone Lucy - Reg. No. 24,735; Steven I. Weisburd - Reg. No. 24,735; Steven I. Weisburd - Reg. No. 24,745; March - Reg. No. 24,735; Steven I. Weisburd - Reg. No. 24,745; March - Reg. No. 24,745; March - Reg. No. 24,745; March - Reg. No. 24,725; No. 24

SEND CORRESPONDENCE TO:

OSTROLENK, FABER, GERB & SOFFEN, LLP 1180 AVENUE OF THE AMERICAS NEW YORK, NEW YORK 10036-8403 CUSTOMER 100 2332

DIRECT TELEPHONE CALLS TO: (212) 382-0700

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may joepardize the validity of the application or any patent issued thereon.

Christian SPETH	INVENTOR STERATURE GUAR		23 MAY . 07
RESIDENCE (City and either State or Foreign Country) DK-3540 Lynge, Denmark	ΚX		Y OF CITIZENSHIP nmark
POST OFFICE ADDRESS Kirkevangen 33, DK-3540 Lyne	ge, Denmark		
FULL NAME OF SECOND JOINT INVENTOR (IF ANY)	INVENTOR'S SIGNATURE		DATE
RESIDENCE (City and either State or Foreign Country)		COUNTR	Y OF CITIZENSHIP
POST OFFICE ADDRESS			
FULL NAME OF THIRD JOINT INVENTOR (IF ANY)	INVENTOR'S SIGNATURE		DATE
RESIDENCE (City and either State or Foreign Country)		COUNTR	Y OF CITIZENSHIP
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☐ CONTINUED ON PAGE 2